AN EPR STUDY OF PORE ACCESSIBILITY IN ARGONNE PREMIUM COAL SAMPLES

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INTRODUCTION

We have recently reported (1) an EPR method developed in this lab to determine the pore size and number distribution in high voltatile bituminous coal in the presence of a swelling solvent by diffusing nitroxide spin probes of different size, shape and reactivity into the swellable pores of coal samples. The same method has also been shown (2) to be useful in estimating the number distribution of accessible reactive sites containing carboxylic acid, phenol and amine substitutents in samples of Mary Lee (A), Black Creek (B), Illinois no. 5 (C) and Illinois no. 6 (D), all high volatile bitumnous coal samples by using small size (~0.7 nm radius) spin probes.

It was observed that the distribution of reactive sites varies substantially. For example, the detected acidic and phenolic sites in (B) and (D) (premium coal sample program) exceeded the detected amine site by approximately an order of magnitude. Sample of (B) possessed the greatest number of reactive acidic and phenolic sites of all the coal samples examined. It was also inferred that the ability for the coal pore to hydrogen bond to a spin probe was shown not to be an important process for incorporating spin probes in (A) and (B) and only a slight factor in samples of (C) and (D).

Unfortunately very little independent studies on pore distribution have been reported for coal samples A, B, C and D. Thus it is not possible to verify various conclusions. To remedy this situation, we have expanded our study to include Blind Canyon and Pittsburgh #8 in addition to the Illinois #6 coal samples from the Argonne Premium Coal Sample Program as well as samples from Illinois #6 (PSOC-1354) and New Mexico (PSOC -311) coals wherein comparisons can be made to other studies. For instances, D. Smith and coworkers (3) have studied extensively the pore size distribution for PSOC-311 and PSOC-1354 coals before exposure to solvents by NMR spin-lattice relaxation methods. In addition, small angle neutron scattering studies of Pittsburgh #8 swelled with different solvents have been carried out by Winans and Thiyagarajan (4) while studies by Larsen and Wernett (5) using gas adsorption techniques have permitted some independent measurements of pore accessibility to various solutes in Illinois #6 coal.

This study reports a spin probe - EPR study of pore size distribution, the basic/acidic reactive site distribution, hydrogen bonding site distribution and the effect of a swelling solvent on Blind Canyon, Pittsburgh #8 and Illinois #6 from the Argonne premium coal sample program and Illinois #6 (PSOC-1354) and New Mexico (PSOC-311) from the Penn State Coal Sample Bank at Penn State University.

EXPERIMENTAL

All coal samples were stored and handled under nitrogen or argon. The procedures for preparing (2) the spin probe doped coal samples and analyzing (1,2) the EPR spectra has been described previously. The ash free percentage by weight values for the coal samples obtained from the Argonne Premium Coal Sample Program are as follows: Illinois #6; C(79%), H(5.6%), O(9.7%), and S(5.4%); Pittsburgh #8; C(83%), H(5.8%), O(8%), and S(1.6%); and Blind Canyon; C(79%), H(6.0%), O(13%) and S(0.5%). The proximate and ultimate analysis for PSOC-1354 and PSOC-311 are available from the Penn State Coal Sample Bank at Penn State University. The spin probes (I-IX) were obtained form Molecular Probes, Inc. Junction City, Oregon. The pore size distribution of the coal samples was studied using spin probes I-V while the basic/acid reactive site distribution was examined by using spin probes VI and VII. To differentiate between hydrogen-bonding to the nitroxyl group and substitutents in the swellable pores of the coal, spin probes VIII and IX were used. The effect of a swelling solvent was demonstrated by swelling samples of Pittsburgh #8 coal with toluene, benzene and pyridine. To reduce the sample uncertainty, Professor D. Smith at the University of New Mexico sent his samples of PSOC-311 and PSOC-1354 so that a direct comparison could be made between our results and those he deduced from NMR studies.

RESULTS

Pore Size Distribution

The relative concentration of incorporated spin probes varied among different coal samples and is given in Table I. The relative spin concentration ratio of spin probes I:II:III:IV:V for Illinois #6 (Argonne) and PSOC-1354 (Illinois #6) equals 5.6:15.6:1.3:1.0: 1.9 and 3.5:25.2:1.0:1.0:3:3 respectively. It is clear that both samples have rather similar pore size distribution except that the Illinois #6 (Argonne) coal sample has a greater number of pores with a radius of 0.67-3.4 nm by a factor of 3 to 7. All the coal samples studied show the highest number of cylindrical pores with a diameter of 0.9 nm. However, compared to other samples, Blind Canyon coal has a quite high number of chain-like pore shapes. On the other hand, Pittsburgh #8 coal shows a pore distribution of largely cylindrical type pore shapes. For the coal samples Illinois #6 (Argonne), PSOC-311, and PSOC-1354, the long chain pore (radius = 1.3 nm) occurs the least number of times whereas for Pittsburgh #8 and Blind Canyon coal the long chain pore with a radius of 3.4 nm occurs the least number of times.

The pore structure of PSOC-311 and PSOC-1354 coal samples has been analyzed by Smith et al. (3) using low field NMR spin lattice relaxation measurements. It is known that the spin lattice relaxation time T_1 of H_2O attached to the pore surface differs from the corresponding T_1 for the bulk H_2O. Furthermore, Smith et al. (3) has shown that pore size determination can be deduced from T_1 measurements. Their results show the number of pores in PSOC-1354 with a radius of 0.5-5.0 nm is greater than that found in PSOC-311. In contrast, our studies show just the opposite trend in the presence of a swelling solvent for each spin probe used. This disagreement can be rationalize as follows. The NMR method measures the total volume of pores available in a particular coal sample. However, the spin probe method determines the pore volume that are accessible to a given spin probe upon swelling with a given solvent. On this basis it is possible to deduce that PSOC-1354 coal has more bottleneck pores (unaccessible to spin probes) than the PSOC-311 coal in the presence of toluene.

Recently Small Angle Neutron Scattering (SANS) studies (6) of the pore shapes and sizes of Illinois #6 coal characterize the pore shapes as elongated voids with an average radius of 2.5 nm. Unfortunately the spin probes used in this study are all smaller than this except for V (3.4 nm). Even so the spin probe study indicates a majority of cylindrical and a substantial number of long chain-like pores occur, in reasonable agreement with the SANS data. (6) It has been shown (7) by use of the SANS method that the shape distribution of the micropore and mesopores in unmodified coal do not change when the coal samples in the dry state are suspend in cyclohexane. Toluene, the swelling solvent used in our studies is considered to be a mild swelling solvent and therefore assumed not to significantly change the pore structure. Previous gas adsorption work (5) in Illinois #6 coal samples suggests that coal pores are mostly closed and inaccessible to molecules such as cyclopropane which are not soluble in the coal.

Reactive Site Distribution

The relative acidic/basic reactive site distributions in various samples of coal were determined using spin probes VI and VII. The results are given in Table 2 where the data is normalized to spin probe VI in Pittsburgh #8. The molecular volume of each spin probe is shown within the parenthesis.

The number ratio of pores containing amine groups to those containing acid or phenolic groups is 1:1.2; 1:3.7; 1:5.4; 4.6:1; 1:2.4 for coal samples PSOC-311, PSOC-1354, Illinois #6 (Argonne), Blind Canyon, and Pittsburgh #8 respectively. It is interesting to note that among the data listed in Table 2, only Blind Canyon coal (a low sulfur coal) has more basic sites than acidic acids within the pores defined by spin labels VI and VII. The presence of acidic sites in Illinois #6 has been confirmed by a small angle neutron scattering study (6).

Degree of Hydrogen Bonding in Swellable Pores

The relative spin concentration obtained for spin probes VIII and IX are depicted in Table 3. The volume of each spin probe is given within the parenthesis. It is apparent from the data given in Table 3, that the presence of an additional site for hydrogen bonding slightly benefits the incorporation of spin probes in PSOC-311 and Blind Canyon coal samples. On the contrary, for coal sample PSOC-1354, the presence of additional site for hydrogen bonding is a significant hinderance for spin probe incorporation. Values for Pittsburgh #8 could not be obtained because the EPR spectrum exhibited very poor resolution. Even though the exact reason for this is not understood, it could be due to the failure to collapse sufficient number of pores around the spin probes before being washed away with ethanol.

Pore Distribution Dependence on Swelling Solvent

In Table 4 are presented the changes in the concentration of spin probes I, II and V as Pittsburgh #8 is swelled with toluene, benzene and pyridine. It is to be noted that as the solvent is changed from benzene to pyridine, the number of spherical pores decreases (i.e. spin probe I) while the number of elogonated pores increase (spin probe II). Generally, toluene is considered a poor swelling solvent relative to pyridine. Thus the accessible pore volume for those solvents which do not disrupt the original coal structure is significantly reduced over that when a solvent like pyridine is used. These results are in agreement with Winans and Thiyagarajan study (4) using small angle neutron scattering techniques to examine the effect of swelling solvent on pore structure. The results of a mild swelling solvent like benzene was compared to an aggressive swelling solvent (pyridine). The pore structure of Pittsburgh #8 in the presence of benzene was found to be roughly spherical whereas in the presence of pyridine, it was found to be elongated. This very nice agreement with an independent measurement suggests that the spin probe EPR measurements are useful indicators of the behavior of coal pores in the presence of various solvents and measure the relative difference in accessible pores on the molecular level.

CONCLUSION

The spin probe - EPR method showed that as the swelling solvent was changed from benzene to pyridine, the number of spherical pores in Pittsburgh #8 decreased while the number of elongated pores of distinct size increased sharply in agreement with previously reported SANS studies (4). Reasonable agreement was found with independent studies (6) on the average size distribution and the presence of acid character in the accessible pores of Illinois #6. Comparison between NMR data and the pore distribution pattern deduced by the spin-probe EPR method indicates that toluene swelled PSOC-1354 has more bottleneck pores with a radius of less than 5 nm which are not accessible to toluene than PSOC-311.

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Table 1. The relative pore size distribution for spin probes I, II, III, IV, and V (toluene swelling solvent).

	I	II	III	IV	V
Radius[a]	0.67 nm	0.90 nm	1.07	1.3 nm	3.4 nm
Molecular Vol.	143.9 $Å^3$	230.7 $Å^3$	308.7 $Å^3$	335.3 $Å^3$	459.1 $Å^3$
Sample	Spherical	Cylindrical	Chain	Long Chain	Long Chain
PSOC-311	48.6	202.6	48.6	7.7	37.7
PSOC-1354	10.2	73.7	2.9	3.0	9.7
ILLINOIS #6	72.3	201.1	17.0	12.8	25.3
BLIND CANYON	15.4	133.0	116.9	70.9	10.3
PITTSBURGH #8	4.0	133.4	1.9	9.3	1.0

(a) Effective radius including Van der Waals nearest approach distance.

Table 2. The relative basic/acid reactive site distributions for spin probes VI and VII (toluene swelling solvent).

Coal Sample	VI (143.6 $Å^3$) Basic sites	VII (131.5 $Å^3$) Acid sites
PSOC 311	16.9	21.2
PSOC 1354	1.6	6.1
Illinois #6	3.1	16.9
Blind Canyon	8.8	1.8
Pittsburgh #8	1.0	2.4

Table 3: Relative sites distribution for spin probes VIII and IX (hydrogen-bonding-differences).

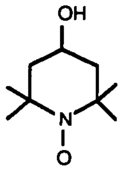
Coal Sample	VIII (138.3 Å^3) (1-H bond site)	IX (138.2 Å^3) (2-H bond sites)
PSOC-311	21.3	37.1
PSOC-1354	25.7	1.0
Illinois #6	3.5	3.7
Blind Canyon	5.7	11.0
Pittsburgh #8	--	---

Table 4. The relative spin probe concentration for probes I, II, III as a function of swelling solvent for Pittsburgh #8 coal.

Spin Probe	Solvent	Spin Probe Concentration Ratio[a]
I	Toluene	4.2
(Spherical)	Benzene	18.8
	Pyridine	1.0
II	Toluene	205
(Cylindrical)	Benzene	348
	Pyridine	2860
V	Toluene	2.0
(Long Chain)	Benzene	5.1
	Pyridine	6.1

(a) normalized to spin probe I in pyridine.

SPIN PROBES I-IX



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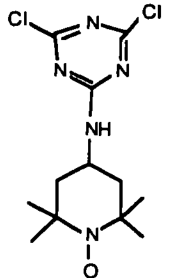

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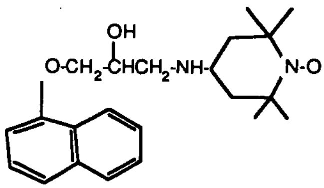

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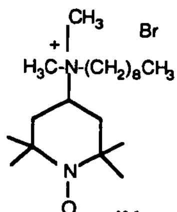

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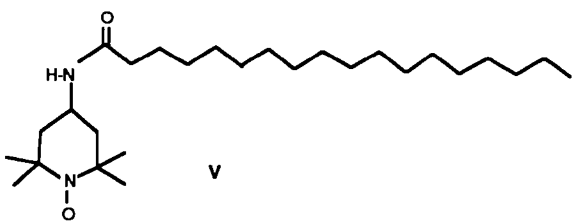

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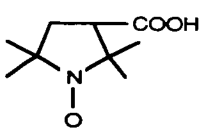

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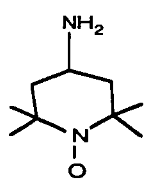

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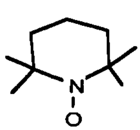

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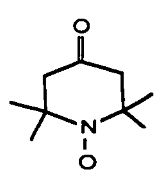

IX